

IMPACT OF ADDITION OF Ca ON CLOGGING OF SEN AND MAGNETIC PROPERTIES OF NON-ORIENTED SILICON STEEL

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Abstract

The submerged entry nozzle (SEN) clogging has been happening during continuous casting (or CC for short) for non-oriented silicon steel. To solve the problem, the paper studied a flow rate through SEN, a node attached to one of them, and the impact on the clogging. The results showed that when SEN is clogged seriously, the casting speed has to decrease below the target casting speed and that SEN clogging can be predicted by comparing the actual value and the theoretical one of a casting speed. Al_2O_3 and its composite inclusions caused the SEN clogging and the addition of Ca can solve SEN clogging during CC of the silicon steel both theoretically and practically. Furthermore, the impact of the addition of Ca on the magnetic properties of the steel were analyzed. The results showed that the core loss and the magnetic induction of the silicon steel decreased by using the addition of Ca, which generated more dissolved Aluminum, and the addition of Ca generated more harmful textures, which reduced the magnetic induction.

Keywords: Addition of Ca; SEN clogging; Magnetic property; Non-oriented silicon Steel.

1. Introduction

SEN clogging always happened during continuous casting for non-oriented silicon steel. Because of SEN clogging, the casting speed decreased, and even the entire casting would be canceled in severe cases. Some scientists who had been working on SEN clogging for years believed that SEN clogging usually happened due to inclusions aggregating, the modification of non-metallic inclusions, electroslag remelting, and multi-holed ceramic filters were the method to resolve the problem [1-9]. During CC of steel for welding wires with higher silicon content, the addition of Ca was not advised despite the fact that it would eliminate some defects of casting process, because it would increase cracking of the steel during the welding [10]. However, there has been no research on the impact of addition of Ca on non-oriented silicon-steel to improve SEN clogging. Moreover, non-oriented silicon steel has unique properties (the magnetic properties, etc.) and its production process is more complicated compared to other steel [11-13]. Therefore, the impact of the addition of Ca on non-

oriented silicon steel is different from other steel, and it is necessary to study it. The paper studied what caused SEN clogging during casting of non-oriented silicon steel, the addition of Ca on solving SEN clogging of non-oriented silicon steel both theoretically and practically, and the impact of the addition of Ca on the magnetic properties (core loss and magnetic induction) of silicon steel.

2. Experimental methods

This paper studied CC of non-oriented silicon steel, whose chemical composition is shown in Table 1. The steelmaking process was BOF (basic oxygen furnace)→RH→CC. The slag thickness before RH was about 80mm, and the slag composition is shown in Table 2. Pure aluminum particles were added into the ladles during RH for deoxidization.

A flow rate during CC was calculated to analyze the bad impact of SEN clogging and to judge if the SEN clogging happens theoretically.

After the casting with 10 heats, SEN clogging happened, and a node attached to the one of them,

Table 1. The chemical elements of the silicon steel slabs (in mass%)

Elements	C	Si	Mn	P	S	Al	N	Ti
mass%	≤0.003	0.85-1.2	0.10~0.35	≤0.03	≤0.0040	0.15~0.40	≤0.004	≤0.003

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Table 2. The slag compositions before RH (in mass%)

Compositions	CaO	SiO ₂	MgO	TFe	P ₂ O ₅	R
mass%	45~50	10~15	5~10	15~20	1.322	2~5

Table 3. The chemical elements of the Si-Ca wires (in mass%)

Elements	Si	Ca	C	Al	P	S	Yield/%	
							Si	Ca
mass%	52.0-62.0	≥24.0	≤1.10	≤2.20	≤0.040	≤0.040	95~97	25~32

which caused the clogging. The node was taken. The node and its sampling method are shown in Figure 1. The sample was analyzed by using SEM and EDS performed manually.

In order to change some properties of inclusions in the liquid silicon steel and to reduce the clogging, the addition of Ca on solving SEN clogging was studied, both theoretically and practically. Si-Ca wires for the addition of Ca were added into the liquid steel at the end of RH, and soft bubble-stirring was applied for 10min. The chemical elements of the Si-Ca wires can be seen in Table 3.

After hot rolling, cold rolling, and annealing, two groups of steel samples were chosen, one using the addition of Ca and the other not using it. Their core loss and magnetic induction were measured by Epstein frame. The composition and textures of the samples were analyzed for explaining the impact of the addition of Ca on the magnetic properties as well. The textures were measured by EBSD (Electron Backscattered Diffraction).

**Figure 1.** A node attached to the SEN causing the clogging (the sample taken in the black circle)

3. Analysis

3.1 Theoretical calculation of the flow rate during casting

A theoretical flow rate of the liquid silicon steel, through SEN, can be calculated by Equation (1), if we suppose the stopper rods were fully open [14]:

$$Q_m = 2\rho_l \pi D^2 \left(\frac{3\alpha gh}{6 + \alpha l} \right)^{\frac{1}{2}} \quad (1)$$

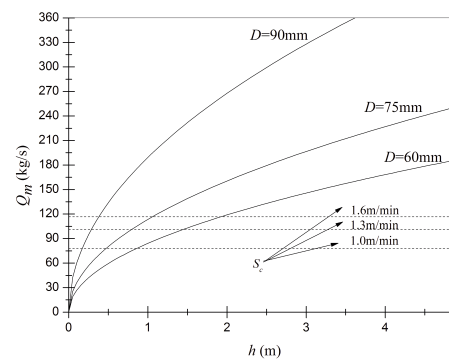
Where Q_m is a flow rate for two strands with two SEN, kg/s. D is the diameter of the nozzles, 0.072m for the mill. ρ_l is the density of the liquid silicon steel, 7000kg/m³ for this case. α is a constant, 1 for the turbulent flow studied. g is the acceleration of gravity. h is a liquid steel level in a ladle, m. l is a friction loss factor, 0.5 for the case.

Suppose the percentage of two stopper rods opening, p_{sn} , were the same at some point. A flow rate through the nozzles Q_{mc} in kg/s, controlled by the stopper rods, can also be expressed by Equation (2).

$$Q_{mc} = w \cdot t \cdot \rho_s \frac{s_c}{30} = p_{sn} \cdot Q_m \quad (2)$$

where w and t are respectively the width and the thickness of the slab, 1.3m and 0.23m for the study. ρ_s is the density of the solid silicon steel, 7797kg/m³ for the case. s_c is a casting speed for two strands, 1.0m/min for the target of this case. Then, based on Equation (2), Q_{mc} should be 77.71kg/s, i.e. 4.66t/min for reaching the target casting speed in the case of the two strands.

As shown in Figure 2 based on Equation (1) and Equation (2), associated with the decrease of the liquid steel level, the flow rate decreases. If D was 90mm, even though the level was obviously below 0.5m, the casting speed could also reach the target of 1.0m/min. And if D was clogged to 60mm, even though the level

**Figure 2.** The relationship between Q_m/s_c and h during casting

was 1m (two times of the level above), the casting speed would not reach the target (only 0.98m/min, i.e. 84.14 kg/s). It indicates that when SEN are clogged seriously, hypothetically the same clogging level for the two nozzles, in order to keep a steady liquid steel level in the tundish, the casting speed has to decrease below the target casting speed.

p_{sn} can be calculated by the following equations:

$$d = \left[r_1^2 - \frac{\pi r_2^2 - a_r}{\pi} \right]^{\frac{1}{2}} - (r_1 - s) \quad (3)$$

$$p_{sn} = \frac{4a_r}{\pi D^2} = \frac{4(r_2^2 - r_1^2 + (d + r_1 - s)^2)}{D^2} \quad (4)$$

where d is a distance the stopper rods move from the closed position, ≤ 0.022 (the effective distance for this study), m. r_1 is the longitudinal section diameter of the stopper rods, 0.053m for the study. r_2 is the cross section diameter of the stopper rods in the closed position, 0.050m for the study. a_r is the area of a annular interspace where liquid steel flows through, under the stopper rods, $\leq \pi D^2/4$, m². s is the depth that the stopper rods insert into the nozzles in the closed position, 0.035m for the study. Based on Equation (1) and Equation (2), p_{sn} can be got:

$$p_{sn} = \frac{w \cdot t}{60\pi D^2} \cdot \frac{\rho_s}{\rho_l} \cdot s_c \left(\frac{3\alpha gh}{6 + \alpha l} \right)^{\frac{1}{2}} \quad (5)$$

Plug the values of the variables for this study, as shown above, into Equation (5), and it can be reduced to:

$$p_{sn} = 3.32 \times 10^{-3} \cdot \frac{s_c h^{\frac{1}{2}}}{D^2} \quad (6)$$

Based on Equation (4) and Equation (6), the following equation can be got:

$$s_c = \left(0.1183 + 3.83 \times 10^2 (d + 0.018)^2 \right) h^{\frac{1}{2}} \quad (7)$$

It can be predicted that if the actual value of s_c is lower than the theoretical one, which can be calculated by Equation (7), and then the clogging in the SEN has been happening.

3.2 Node analysis

As shown in Figure3, all the areas in the sample contained Al₂O₃. A small number of pure Al₂O₃ areas and CaO areas were also observed. It was believed that the sample formed by gathering inclusions that generated from deoxidization and addition of the [Al] (for meeting performance requirements of the silicon steel) by using Al-alloy, and from the reaction between Al₂O₃ and slag/furnace lining (Al₂O₃-MgO-C bricks or MgO-C bricks shown above). Only Al₂O₃, CaO, and MgO were calculated, and the mole composition and the state (liquid or solid) of the areas analyzed are shown in Figure 4. It can be indicated that almost all the areas (98%, 42 of 43) were solid at the casting temperature (1530°C/1803K). Therefore, the node that included inclusions with high melting-points caused the SEN clogging.

The molecular ratios of the CaO/Al₂O₃ are shown in Figure 5. An inclusion mainly including CaO-Al₂O₃ would become liquid with its molecular ratio being 1.7 or 3 during casting of steel at a temperature above 1500°C [16]. However, from the figure it can be seen that most of the areas are not 12CaO·7Al₂O₃ (or C12A7 for short, whose melting point is the lowest in CaO-Al₂O₃ inclusions) or 3CaO·Al₂O₃ (or C3A for short). Therefore, the addition of Ca can be used to prevent a node from happening by transforming high melting-point inclusions into C12A7 in the liquid silicon steel, and to improve the SEN clogging.

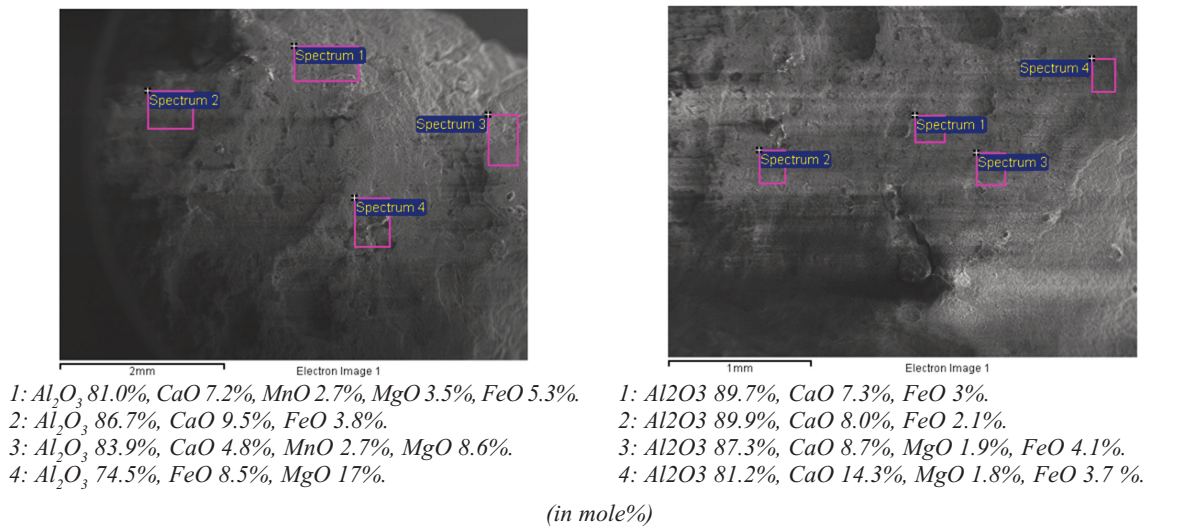


Figure 3. SEM-EDS analysis for the node



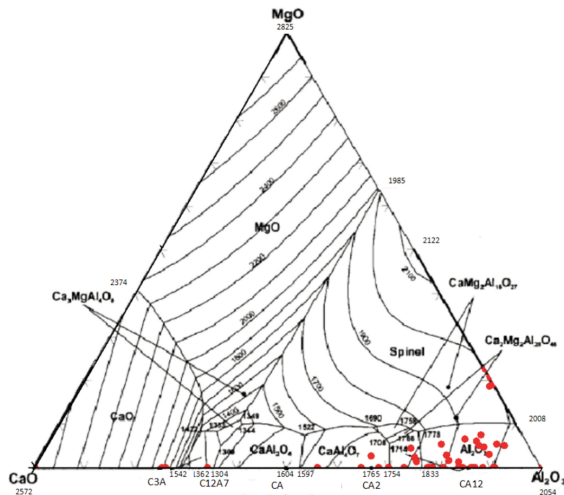


Figure 4. The areas analyzed in the sample in the Al_2O_3 -CaO-MgO diagram with the isograms of the melting points [15]

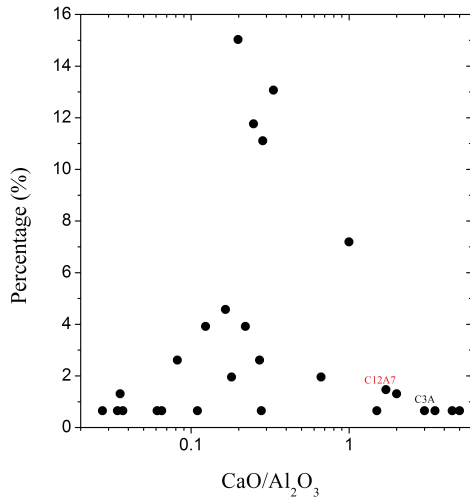
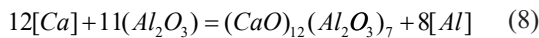


Figure 5. The number percentages of the areas analyzed with the different CaO/Al_2O_3 in the sample

3.3 Thermodynamic calculation of the addition of Ca

For this study of the addition of Ca, only C12A7 is dealt with. C12A7 formed by the reaction of Ca plus Al_2O_3 is shown in Equation (8) [16]:



Supposed that all oxides reacted with [Ca] was Al_2O_3 , and then the rate of Ca in liquid steel (Ca_{Re} in ppm), for the reaction of Equation (8), can be calculated by the following Equation:

$$Ca_{Re} = \frac{4Ar_{Ca}}{11Ar_O} (O_T - [O]) = 0.909 \left(O_T - 1.74 \times 10^{-1} w[Al]^{-\frac{2}{3}} \right) \quad (9)$$

Where Ar_{Ca} and Ar_O are respectively the atomic mass of Ca and O. O_T is the total oxygen, which includes the oxygen in oxides and the dissolved oxygen, in the liquid steel, ppm. [O] is the dissolved oxygen, ppm. The total Ca in the liquid steel (in ppm) can also be divided into two parts we refer to as Ca_{Re} and the Ca at equilibrium (in ppm).

When the reaction is at equilibrium, the relationship between [Al] and [Ca] or [O] will be $w[Ca] = 1.26 \times 10^{-2} w[Al]^{2/3}$ or $W[O] = 1.74 \times 10^{-5} w[Al]^{-2/3}$, according to the thermodynamic data and Equation (8) [17]. $w[Ca]$ and the total Ca for forming C12A7 can be calculated by measuring $w[Al]$ before the addition of Ca.

And then, the Si-Ca wires (M_{Si-Ca} in kg) and their total length (L_{Si-Ca} in m) used for addition of Ca per heat can be calculated by Equation (10). Too much or too little [Ca] will form other high melting point inclusions.

$$L_{Si-Ca} = \frac{4}{\pi D_{Si-Ca}^2} \cdot \frac{M_{Si-Ca}}{w[Si]\rho_{Si} + w[Ca]\rho_{Ca}} = \frac{4M_{Lc}}{ay\pi D_{Si-Ca}^2 (w[Si]\rho_{Si} + w[Ca]\rho_{Ca})} \left[\frac{1.26 \times 10^{-4} w[Al]^{2/3} + 9.09 \times 10^{-7}}{\left(O_T - 0.174 w[Al]^{-\frac{2}{3}} \right)} \right] \quad (10)$$

Where M_{Lc} is the capacity of a ladle, 2.1×10^5 kg for the study. a is the mass percentage of Ca in a Si-Ca wire, 30% for the study. y is the yield of Ca in a Si-Ca wire in liquid steel, 28% for the study. D_{Si-Ca} is the diameter of a Si-Ca wire, 0.013m for the study. ρ_{Si} is the density of Si, 2330 kg/m³. ρ_{Ca} is the density of Ca, 1550 kg/m³.

On the basis of Equation (10), as shown in Figure 6, it can be indicated that under a O_T or $w[Al]$, the more $w[Al]$ or O_T is in the liquid silicon steel before addition of Ca, the more Si-Ca wires will be needed for the addition of Ca. Furthermore, more Si-Ca wires are needed to add into the liquid silicon steel for the addition of Ca than other steel, because of higher [Al] in the silicon steel.

4 Verification tests in steel mill

4.1 Addition of Ca for improving SEN clogging of silicon steel

In order to verify the theoretical analysis mentioned above and to prevent the SEN from clogging during CC of the silicon steel, some tests were done.

The quantity of Si-Ca wires added into the liquid silicon steel for a heat was based upon the theoretical

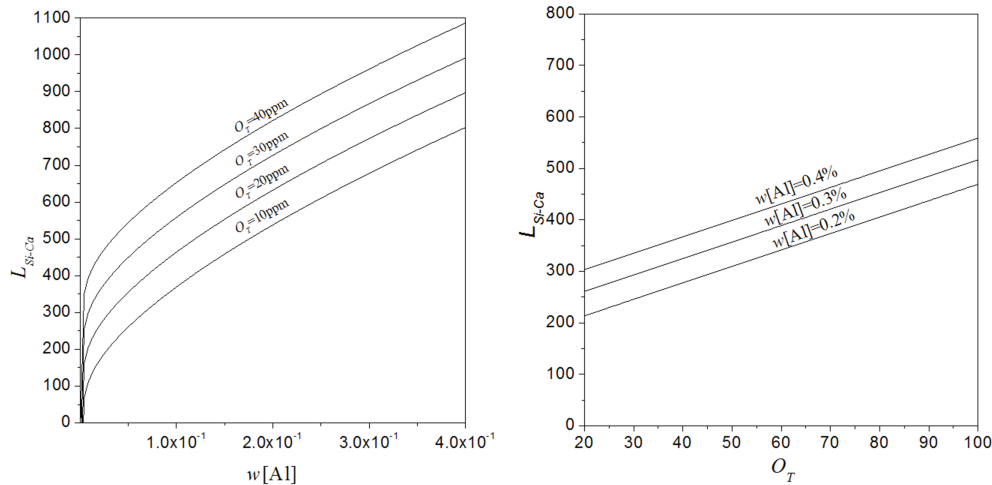


Figure 6. The relationship between L_{Si-Ca} and $w[Al]/O_T$

analysis. 20 castings with addition of Ca were tested in 45 days, and $[Al]$ was 0.20% ~0.35% with 10~30ppm of $[O]$. If a casting was not clogged, 3 steel samples for the heat were taken. If the casting was clogged, the nodes were taken. And 60 steel samples were actually taken. 25 fields of view (or FOV for short) were observed randomly for one sample. The biggest length of an inclusion was defined as the size of the inclusion. And 898 inclusions were analyzed in total. The results showed that by using the addition of Ca, most of the inclusions were transformed into C12A7 and C3A2, and their sizes were between $2\mu m$ and $5\mu m$ as shown in Figure 7 and Figure 8. And SEN clogging did not happen in the 20 casting with the addition of Ca, whose impact was obvious in contrast to the nozzle clogging rate of 2.54% without the addition of Ca .

4.2 Impact of the addition of Ca on magnetic properties of silicon steel

After steelmaking with or without the addition of

Ca, hot-rolling, cold-rolling and annealing, the steel slabs were transformed into the steel sheets. By analyzing the steel sheet samples, it was shown that

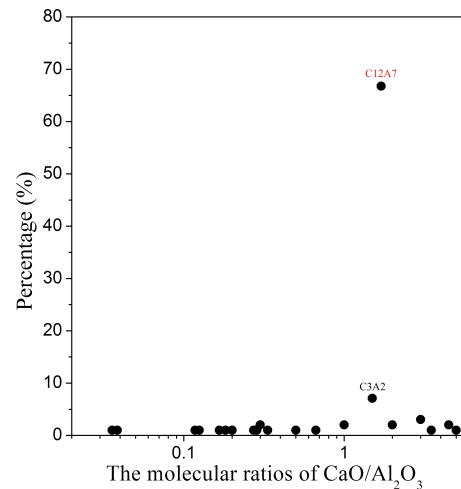


Figure 8. The number percentages of inclusions with different CaO/Al_2O_3 by using addition of Ca

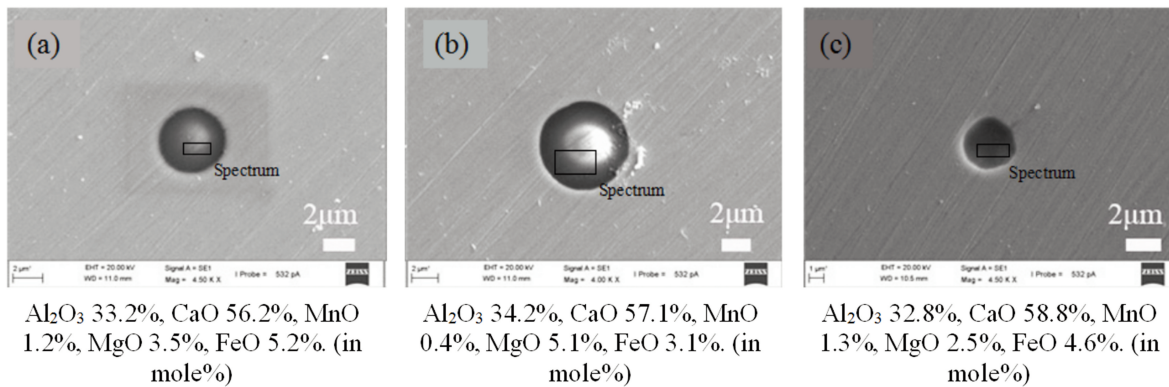


Figure 7. Inclusions after addition of Ca



the core loss and the magnetic induction of the silicon steel was slightly lowered by using the addition of Ca, as shown in Figure 9. There were more Als in the steel using the addition of Ca, which decreased the core loss and the the magnetic induction [18]. It could be explained that the more C12A7 would bring the more Als/ [Al] based on Equation (8).

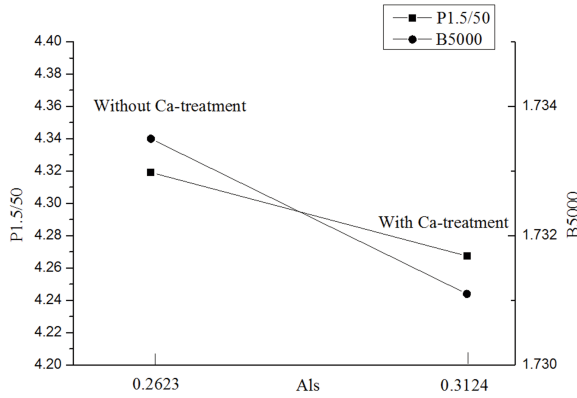


Figure 9. Magnetic properties and Als of the silicon steel with or without the addition of Ca, on average

In Figure 10, {100} planar-texture as shown in purple and {110}<001> texture as shown in bright red were beneficial for the magnetic induction of silicon steel [19]. {111}<112> texture as shown in blue and {111}<110> texture as shown in dark red were harmful for the magnetic induction [19]. There

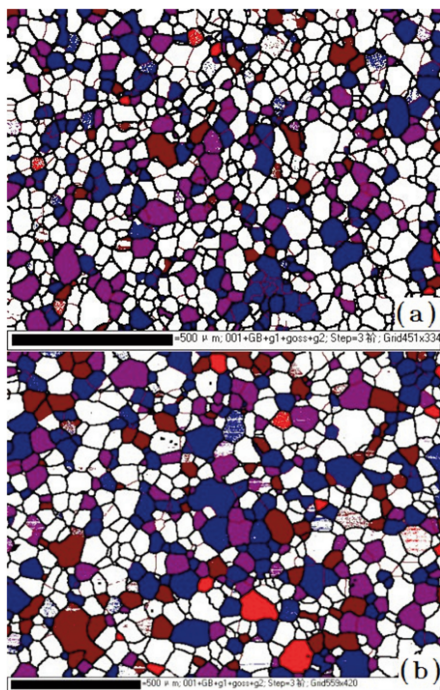


Figure 10. Texture Orientation Distribution: (a) with the addition of Ca, (b) without the addition of Ca

were more {110}<001> texture and {111}<110> texture in the sample without the addition of Ca than that with the addition of Ca.

Based on comprehensive comparison among Figure 10, Figure 11 and Figure 12, it could be seen that most of the textures were {111}<112> texture in both of the samples. The percentages of the different textures in the samples were calculated by using Channel5, as shown in Table 4. From the table, it could be seen that though the harmful textures in the sample with the addition of Ca were little less than that without the addition of Ca, the ratio of (harmful textures)/(beneficial textures) of the sample with the addition of Ca was higher. It was indicated that on the whole, the addition of Ca could bring more harmful textures, which were caused by Als, therefore the magnetic induction of the silicon steel decreased with it.

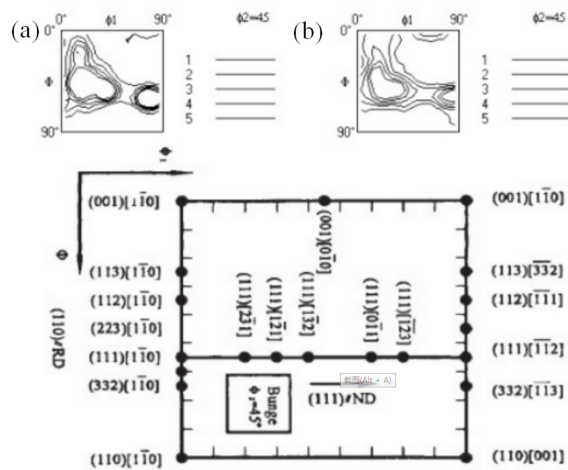


Figure 11. Orientation Distribution Function (ODF): (a) with the addition of Ca, (b) without the addition of Ca

5. Conclusions

This paper studied the reason why the addition of Ca was used in the silicon steel and the impact of the addition of Ca on the silicon steel. It can be concluded that:

The node were Al₂O₃-based substances and solid at the casting temperature, which caused the SEN clogging during CC of the silicon steel; the addition of Ca can solve the SEN clogging both theoretically and practically.

The core loss and the magnetic induction of the silicon steel decreased by using the addition of Ca, which generated more Als; the addition of Ca could bring more harmful textures, which reduced the magnetic induction.



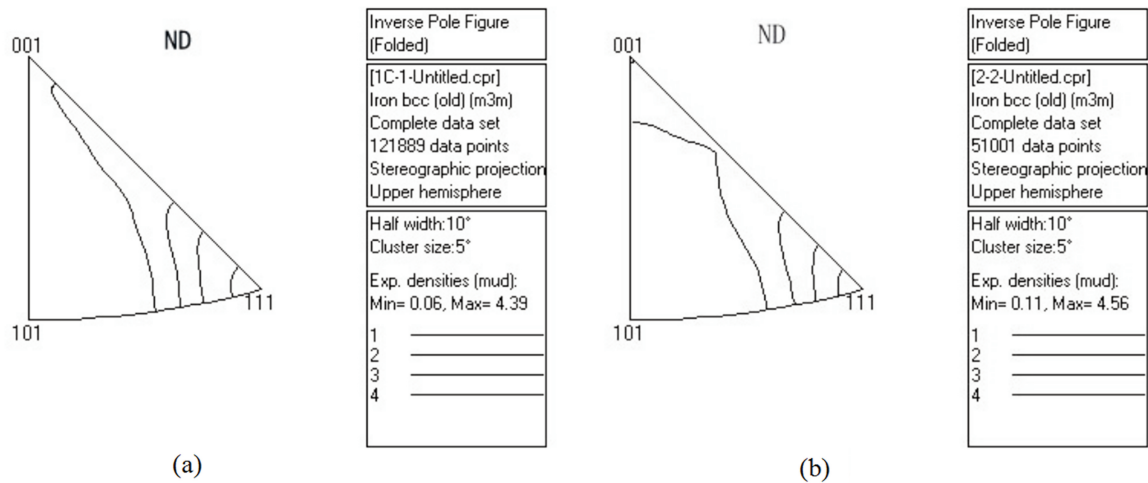


Figure 12. Inverse pole figure: (a) with the addition of Ca, (b) without the addition of Ca

Table 4. Percentages of the different textures in the samples

Process	Beneficial texture, %			Harmful texture, %			Harmful texture / Beneficial texture
	{100}	Goss texture	Total	{111}<112>	{111}<110>	Total	
With addition of Ca	9.1	0.3	9.4	18.2	8.1	26.3	2.8
Without addition of Ca	12.2	1.6	13.8	17.4	7	24.4	1.8

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UTICAJ DODAVANJA Ca NA ZAČEPLJENJE SEN I MAGNETNE OSOBINE NEORIJENTISANOG SILICIJUMSKOG ČELIKA

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Apstrakt

Začepljenje uronjene ulazne mlaznice (SEN) se dešava tokom kontinualnog livenja (skraćeno CC) neorijentisanog silicijumskog čelika. Da bi se taj problem rešio, u ovom radu se proučava protok kroz uronjenu ulaznu mlaznicu, čvor pričvršćen za jednu od mlaznica, i uticaj koji ima na začepljenje. Rezultati su pokazali da kada je mlaznica ozbiljno začepljena, brzina livenja mora da bude manja od ciljane brzine, i da se začepljenje mlaznice može predvideti poređenjem stvarne i teoretske vrednosti brzine livenja. Al_2O_3 i njegove kompozitne inkluzije prouzrokuju začepljenje mlaznice. Dodavanje Ca može rešiti začepljenje mlaznice tokom kontinualnog livenja silicijumskog čelika i teoretski i praktično. Analiziran je i uticaj dodavanja Ca na magnetne osobine čelika. Rezultati su pokazali da se gubitak magnetiziranja i magnetne indukcije silicijumskog čelika smanjivao dodavanjem Ca, što je generisalo više otopljenog aluminijuma; dodavanje Ca je generisalo više štetnih tekstura, što je smanjilo magnetnu indukciju.

Cljučne reči: Dodavanje Ca; Začepljenje uronjene ulazne mlaznice; Magnetne osobine; Neorijentisani silicijumski čelik.

